

We claim:

1. A gas separation process, comprising:

(a) providing a membrane having a feed side and a permeate side and comprising;

(i) a base membrane comprising a selective layer of a first polymer on the feed side, and

(ii) a C₃₊ hydrocarbon-resistant coating layer of a second polymer coating the base membrane on the feed side;

wherein, when measured under the same conditions and in the absence of C₃₊ hydrocarbons, the first polymer has a higher hydrogen/methane selectivity and a lower hydrogen permeability than the second polymer; and

wherein the second polymer has a fractional free volume no greater than about 0.3 and a glass transition temperature of at least about 100°C, and is chosen from the group consisting of (I) polymers comprising repeating units having a fluorinated cyclic structure of an at least 5-member ring and (II) polymers having a ratio of fluorine to carbon atoms in the polymer greater than 1:1;

(b) passing a gas mixture comprising a first gas that is not a C₃₊ hydrocarbon, a second gas that is not a C₃₊ hydrocarbon and a C₃₊ hydrocarbon across the feed side;

(c) providing a driving force for transmembrane permeation;

(d) withdrawing from the permeate side a permeate stream enriched in the first gas compared to the gas mixture;

(e) withdrawing from the feed side a residue stream depleted in the first gas compared to the gas mixture.

2. The process of claim 1, wherein the first gas is selected from the group consisting of hydrogen and carbon dioxide.

3. The process of claim 1, wherein the second gas is selected from the group consisting of methane, ethane and ethylene.

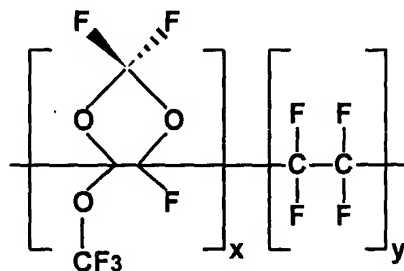
4. The process of claim 1, wherein the gas mixture is a refinery gas stream.

5. The process of claim 1, wherein the gas mixture is a petrochemical plant gas stream.

6. The process of claim 1, wherein the gas mixture is natural gas.

7. The process of claim 1, wherein the gas mixture is associated gas.

8. The process of claim 1, wherein the second polymer is formed from a monomer selected from the group consisting of fluorinated dioxoles and fluorinated dioxolanes.
9. The process of claim 1, wherein the second polymer comprises a copolymer.
10. The process of claim 1, wherein the second polymer has the formula:



where x and y represent the relative proportions of the dioxole and the tetrafluoroethylene blocks, such that $x + y = 1$.

11. The process of claim 1, wherein the second polymer has a propane permeability as measured at 25°C with pure propane of no greater than about 20 Barrer, a methane permeability as measured at 25°C with pure methane of at least about 5 Barrer, and a hydrogen permeability as measured at 25°C with pure hydrogen of at least about 50 Barrer.
12. The process of claim 1, wherein the second polymer has an n-butane permeability as measured at 25°C with pure n-butane of no greater than about 5 Barrer.
13. The process of claim 1, wherein the base membrane is an integral asymmetric membrane.
14. The process of claim 1, wherein the base membrane is a composite membrane.
15. The process of claim 1, wherein the first polymer is selected from the group consisting of polysulfone, cellulose acetate, polyamide, polyaramid, polyimide, polyetherimide, polyester, polycarbonate, polyvinylidene fluoride, polypropylene, polyethylene or polytetrafluoroethylene.
16. The process of claim 1, wherein the gas mixture, as brought into contact with the feed side, has a total C₃₊ hydrocarbons partial pressure of at least about 50 psia.
17. The process of claim 1, wherein the gas mixture, as brought into contact with the feed side, has a carbon dioxide partial pressure of at least about 50 psia.
18. The process of claim 1, wherein the membrane provides a pressure-normalized hydrogen flux when in use in the process of at least about 50 GPU.

19. The process of claim 1, wherein the membrane provides a pressure-normalized carbon dioxide flux when in use in the process of at least about 50 GPU.
20. The process of claim 1, further comprising passing the permeate stream to additional separation treatment.
21. The process of claim 1, further comprising passing the residue stream to additional separation treatment.
22. The process of claim 1, wherein the membrane exhibits a mixed-gas selectivity for hydrogen over methane as measured at the operating conditions of the process of at least about 20.
23. The process of claim 1, wherein the membrane exhibits a mixed-gas selectivity for carbon dioxide over methane as measured at the operating conditions of the process of at least about 15.
24. The process of claim 1, wherein the gas mixture comprises a process or off-gas stream from a hydroprocessor.
25. The process of claim 1, wherein the gas mixture comprises a process or off-gas stream from a catalytic reformer.
26. The process of claim 1, wherein the gas mixture comprises a process or off-gas stream from a fluid catalytic cracker.
27. The process of claim 1, wherein the gas mixture comprises a process or off-gas stream from a steam cracker.
28. The process of claim 1, wherein the gas mixture comprises a process or off-gas stream from a steam reformer.
29. The process of claim 1, wherein the gas mixture comprises natural gas.
30. The process of claim 1, wherein the gas mixture comprises associated gas.
31. The process of claim 1, further comprising removing a contaminant material that has been brought into a module housing the separation membrane during operation of steps (a) through (d) by:
 - (f) discontinuing steps (b) through (e); and
 - (g) flushing the module with an organic solvent.

32. A separation membrane, comprising:

(a) a base membrane having a feed side and a permeate side, and comprising a polymeric selective layer on the feed side,

wherein the base membrane exhibits:

(i) a first selectivity for a first gas over a second gas under a set of operating conditions and in the absence of C_{3+} hydrocarbons, and

(ii) a second selectivity for the first gas over the second gas under the same set of operating conditions as in (i) but in the presence of C_{3+} hydrocarbons,

wherein the second selectivity is lower than the first selectivity; and

(iii) a first pressure-normalized flux for the first gas under the set of operating conditions and in the absence of C_{3+} hydrocarbons;

(b) a C_{3+} hydrocarbon-resistant polymeric coating layer coating the base membrane on the feed side, wherein the polymeric coating layer comprises a polymer chosen from the group consisting of (i) polymers comprising repeating units having a fluorinated cyclic structure of an at least 5-member ring, the polymers having a fractional free volume no greater than about 0.3, and (ii) polymers having (A) a ratio of fluorine to carbon atoms in the polymer greater than 1:1;

(B) a fractional free volume no greater than about 0.3; and

(C) a glass transition temperature of at least about 100°C;

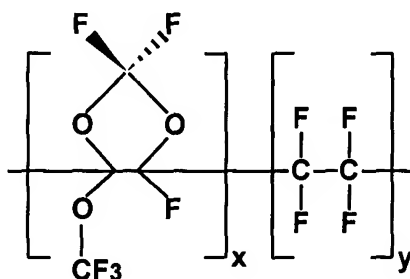
and wherein the gas separation membrane exhibits:

(i) a third selectivity for the first gas over the second gas under the same set of operating conditions and in the presence of C_{3+} hydrocarbons that is higher than the second selectivity and at least about 70% of the first selectivity, and

(ii) a second pressure-normalized flux for the first gas under the same set of operating conditions and in the presence of C_{3+} hydrocarbons that is at least about 70% of the first pressure-normalized flux.

33. The membrane of claim 32, wherein the polymeric coating layer comprises a perfluorinated polymer.

34. The membrane of claim 32, wherein the polymeric coating layer comprises a polymer formed from a fluorinated dioxole monomer.
35. The membrane of claim 32, wherein the polymeric coating layer comprises a polymer formed from a fluorinated dioxolane monomer.
36. The membrane of claim 32, wherein the polymeric coating layer comprises a copolymer.
37. The membrane of claim 32, wherein the polymeric coating layer comprises a copolymer formed from fluorinated dioxole and tetrafluoroethylene repeat units.
38. The membrane of claim 32, wherein the polymeric coating layer comprises a polymer having the formula:



where x and y represent the relative proportions of the dioxole and the tetrafluoroethylene blocks, such that $x + y = 1$.

39. The membrane of claim 32, wherein the base membrane is an integral asymmetric membrane.
40. The membrane of claim 32, wherein the base membrane is a composite membrane.
41. The membrane of claim 32, wherein the polymeric selective layer comprises a glassy polymer.
42. The membrane of claim 32, wherein the polymeric selective layer comprises a polymer selected from the group consisting of polysulfone, cellulose acetate, polyamide, polyaramid, polyimide, polyetherimide, polyester, polycarbonate, polyvinylidene fluoride, polypropylene, polyethylene or polytetrafluoroethylene.
43. The membrane of claim 32, wherein the polymeric selective layer comprises a polyimide.
44. The membrane of claim 32, in the form of a flat sheet.
45. The membrane of claim 32, in the form of a hollow fiber.